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TRANSPORT BEHAVIOR OF MULTIVALENT BETA ALUMINAS(U)
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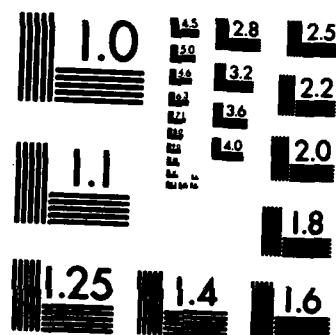
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Contract N00014-83-K-0498

Technical Report No. 1

Transport Behavior of Multivalent Beta'' Aluminas

by

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Prepared for Publication in the
Conference Proceedings on
High Temperature Solid Oxide Electrolytes
Symposium, New York

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May, 1984

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER One (1)	2. GOVT ACCESSION NO. A142,968	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Transport Behavior of Multivalent Beta" Aluminas		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) B. Dunn and G.C. Farrington		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0498
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept of Materials Science and Engr. University of California, Los Angeles Los Angeles, CA 90024		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217		12. REPORT DATE May 1984
		13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Detachment 1030 East Green St. Pasadena, CA 91106		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ion exchange reactions were used to substitute divalent and trivalent cations for the entire sodium ion content of sodium beta" alumina. A wide range of divalent and trivalent beta" aluminas were synthesized which exhibited conductivities much greater than any other divalent or trivalent solid electrolyte in the 300-400°C range. The multivalent beta" aluminas greatly extend the oppor- tunities for electrochemical sensors based on solid electrolytes.		

TRANSPORT BEHAVIOR OF MULTIVALENT BETA" ALUMINAS

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ABSTRACT

Ion exchange reactions were used to substitute divalent and trivalent cations for the entire sodium ion content of sodium beta" alumina. A wide range of divalent and trivalent beta" aluminas were synthesized which exhibited conductivities much greater than any other divalent or trivalent solid electrolyte in the 300-400°C range. The multivalent beta" aluminas greatly extend the opportunities for electrochemical sensors based on solid electrolytes.

I. INTRODUCTION

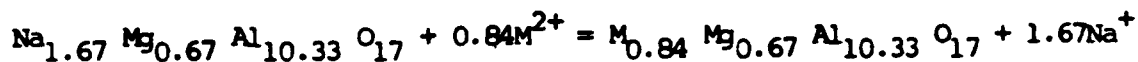
The phenomenon of high cationic conductivity in solids has been largely confined to materials which transport monovalent cations such as Na⁺, Li⁺, K⁺, Ag⁺ and H⁺. Numerous studies have established that these solids are capable of achieving appreciable conductivities ($10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$) in the temperature range 25 to 300°C. In contrast, divalent cation conduction is a process which, if it occurs at all, is observed at elevated temperatures. Even beta alumina, a structure which is a versatile and conductive host to many monovalent cations, exhibits very limited divalent cation transport (1). Thus, we were surprised to discover that beta" alumina is an excellent host for divalent cation conduction (2). A variety of divalent beta" aluminas have been synthesized and all of the compositions possess conductivities of at least $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 300°C. These values are substantially greater than that reported for any other divalent solid electrolyte in this temperature range.

The ability of the beta" alumina structure to permit rapid divalent cation motion demonstrates that the phenomenon of fast ion transport in solids is not restricted to selected monovalent cations. In fact, recent results indicate that the beta" aluminas are also capable of supporting trivalent cation motion. The advent of these materials greatly extends the range and possibilities of electrochemical sensors based on solid electrolytes. In this paper we review the synthesis, properties and structure of this new family of compounds. Although some of this work was published in a previous paper (3), we will emphasize the more recent results on thermodynamics, structure and transport properties.

II. DIVALENT BETA" ALUMINAS

A. Preparation

The divalent beta" aluminas are derivatives of sodium beta" alumina in which the entire sodium ion content has been replaced by divalent cations. The materials were prepared by the ion exchange of single crystals of Na⁺ beta" alumina using appropriate molten salts. The starting crystals were grown by a flux evaporation method and possessed compositions of about Na_{1.67}Mg_{0.67}Al_{10.33}O₁₇ as determined by chemical analysis. Radiochemical and/or gravimetric methods were used to determine the extent of ion exchange. The weight change was consistent with the concept that two sodium ions were replaced by one divalent ion;



Specific aspects of the experimental procedures were described previously (3).

A variety of divalent beta" aluminas have been synthesized with compositions based on divalent cations from Groups IIa (Ca²⁺, Sr²⁺, Ba²⁺), IIB (Zn²⁺, Cd²⁺, Hg²⁺), IVa (Sn²⁺, Pb²⁺) and VIb (Mn²⁺). The preparation of these materials was generally quite direct, although some difficulties did arise when high vapor pressure salts or mixed valences were involved (3). Experimental conditions for achieving complete divalent ion exchange are listed in Table 1 for some representative compounds. The rate of ion exchange was usually quite rapid, an indication of fast divalent cation motion. Complete exchange generally occurred much sooner than the conditions listed in Table 1. For example, Pb²⁺, Sr²⁺ and Ba²⁺ beta" alumina compositions were produced after a 1 hour immersion in their respective salts at 550°C. Complete Sn²⁺ replacement was observed after only 15 minutes in molten SnCl₂ at 500°C. The rate of ion exchange has been used to determine the diffusion coefficient for some divalent cations (Section II.D). In addition to rapid divalent cation replacement, we also found that the exchange reaction was fully reversible. Divalent beta" aluminas were re-exchanged back to the sodium isomorph when immersed in a NaCl-NaNO₃ melt under similar exchange conditions as the divalent ion exchange (2). Finally, it is important to distinguish between the exchange characteristics of beta and beta" alumina. As first reported by Yao and Kummer (1), divalent ion exchange in beta alumina is a slow process which generally results in partial replacement. The very different response of beta and beta" aluminas to divalent ion motion reflects the particular transport mechanisms operable in these structures (3,4).

B. Thermodynamics of Ion Exchange

The ability to easily synthesize the divalent compositions and the reversibility of these reactions has led us to investigate the thermodynamics of the ion exchange process. The only previous work in this area is that of Yao and Kummer (1) who considered the Na⁺ → K⁺ exchange in beta alumina. Griep et al. (5) recently considered the monovalent to divalent exchange in beta" alumina using K⁺ and Na⁺ beta" aluminas as the starting materials for synthesizing Cd²⁺ and Pb²⁺ beta" aluminas. The standard free energy for the exchange reaction was calculated at various melt compositions by determining

the difference in chemical potentials for the ionic species in both the liquid and solid phases. This approach is rather different from that of Yao and Kummer whose exchange reaction implied that substantial chemical changes were occurring in the melt during ion exchange. In actuality, there is a large excess of melt during the ion exchange treatment and the melt composition is virtually unaffected by the exchange process. Thus, the chemical potential approach more closely follows the experimental aspects of ion exchange.

The values for the standard free energy of ion exchange were found to be in the range of -8000 to -15,000 cal/mole at $\sim 1000^\circ\text{K}$ and indicate that there is a strong thermodynamic driving force for complete divalent ion replacement. (5) Chemical potentials calculated for Pb in the $2\text{K}^+ \rightarrow \text{Pb}^{2+}$ exchange are shown in Fig. 1. The large chemical potential gradient explains why this exchange occurs so readily. When a crystal of K^+ beta" alumina is immersed in PbCl_2 , Pb^{2+} will tend to diffuse from high chemical potential (the liquid) to low (the solid). The process continues until equilibrium is attained, i.e. the same chemical potential for Pb in both liquid and solid phases. It should be recognized that there are no kinetic barriers to divalent ion motion at these temperatures (Section II.d), thus enabling the exchange reaction to proceed to equilibrium. The good agreement for the chemical potentials shown in Fig. 1 for Pb in the melt and solid phases serves to verify the calculation method used in the analysis.

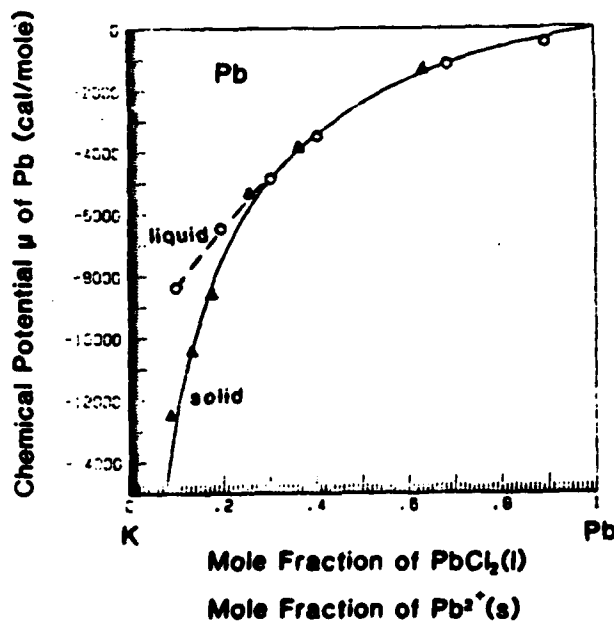


Fig. 1 Chemical potential for Pb in the chloride melt and in beta" alumina for the K^+ to Pb^{2+} exchange.

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Table 1

Conditions for Complete Divalent
Ion Exchange in Beta" Alumina

Ion	Melt Composition(mole%)	Temperature(°C)	Time(hr)
Sr ²⁺	47Sr(NO ₃) ₂ -53SrCl ₂	550	20
Ba ²⁺	62Ba(NO ₃) ₂ -38BaCl ₂	550	20
Cd ²⁺	CdCl ₂	600	20
Hg ²⁺	HgCl ₂	280	25
Sn ²⁺	SnCl ₂	500	0.5
Pb ²⁺	PbCl ₂	525	20

Table 2

Ionic Distributions in Multivalent Beta" Aluminas(6)

Ion	Ionic Radius($\overset{\circ}{\text{A}}$)	C($\overset{\circ}{\text{A}}$)	Occ(6c)	Occ(6c')	Occ(9d)
Zn ²⁺	0.74	33.517	30.7%	25.0%	10.3%
Cd ²⁺	0.95	33.146	26.3	19.3	17.1
Ca ²⁺	1.00	33.270	33.8	16.5	14.9
Sr ²⁺	1.18	33.720	20.4	12.7	17.5
Pb ²⁺	1.19	33.967	46.3	33.7	2.8
Ba ²⁺	1.35	34.084	55.0	8.8	-
Gd ³⁺	0.94	33.134	1.4	-	18.8

C. Structure of Divalent Beta" Aluminas

Thomas and co-workers (6) recently completed single crystal x-ray diffraction studies for several divalent beta" aluminas (Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Zn^{2+}). Refined occupations at the 6c (BR-type) and 9d(mO-type) sites were found to be quite different across the series (Table 2). The authors noted that some degree of non-centrosymmetry existed in all of the divalent compounds. This feature is shown by the difference in the site occupation of adjacent 6c-sites, i.e., 6c and 6c' (Table 2). When the occupation ratio, $\text{occ}(6\text{c})/\text{occ}(6\text{c}')$, is close to unity, the ionic distribution approaches centrosymmetry. This situation occurs with Zn^{2+} , Cd^{2+} and Pb^{2+} beta" aluminas. Ions with the greatest asymmetry, Sr^{2+} and Ba^{2+} , also possess the largest mid-oxygen (mO) occupation. This is apparently not related to an ionic size effect. Sr^{2+} beta" alumina exhibits a large mid-oxygen occupation (17.5%) compared to that of Pb^{2+} beta" alumina (2.8%), despite the fact that the ionic radii for these two ions are within 5%. The authors proposed that both the degree of acentricity as well as the mid-oxygen occupation were important considerations in the transport behavior of the various divalent cations. In addition, they suggested that the variation in c-axis lattice parameter (Table 2) was related to the degree of disorder in the position of the O(5) column oxygen. The c-axis value is a minimum for Cd^{2+} compounds and then expands for both the smaller Zn^{2+} ion as well as for larger ions such as Ba^{2+} and Pb^{2+} (3). These structural studies are significant in that they represent the first attempt to identify the structural factors which enable divalent cations to diffuse so much more rapidly in beta" alumina than in any other host material.

D. Transport Properties

A.C. conductivity measurements have been made on the various divalent beta" aluminas. Most of the compositions are within the range of values shown for Ca^{2+} , Sr^{2+} and Ba^{2+} beta" aluminas (Fig. 2). These conductivities (10^{-2} to 10^{-3} ohm $^{-1}$ cm $^{-1}$ at 300°C) are substantially greater than that of any other divalent solid electrolyte (7). Although these divalent compounds are not nearly as conductive as Na $^{+}$ beta" alumina, there is one divalent composition which does exhibit considerably greater conductivity. The conductivity of Pb^{2+} beta" alumina at 40°C is 10^3 times larger than the other divalent beta" aluminas and only slightly less than the Na $^{+}$ isomorph. In addition, the conductivity for both Na $^{+}$ and Pb^{2+} compositions is virtually identical over the temperature range 0 to -90°C.

The exceptional conductivity for Pb^{2+} ions in beta" alumina is not altogether unexpected. Among the classical halide salts, the only divalent cation to have a measurable diffusivity is Pb^{2+} (in PbI_2 and PbCl_2). Nonetheless, the values in these solids are some 10^6 times less than that of Pb^{2+} in beta" alumina (at 300°C) and underscores the unique transport behavior of the beta" alumina structure. The high electronic polarizability of the Pb^{2+} ion is undoubtedly beneficial for ion transport. Furthermore, the numerous electron shells of the Pb^{2+} ion may effectively screen the nucleus and reduce the strength of the long range coulombic interactions between Pb^{2+} and the surrounding anions and vacancies (7). Finally, the recent structural evidence suggests that the short range structure in Pb^{2+} beta" alumina is the most

favorable one for divalent cation motion (6).

All of the conductivity measurements to date involve a.c. impedance techniques which are not ion specific. To verify that ion transport in the divalent beta" aluminas is from divalent cation motion, ionic diffusion during the ion exchange process was investigated. Radiotracer techniques with Sr^{2+} (7) and gravimetric methods with Zn^{2+} (8) were used to obtain diffusion coefficients for these divalent cations in beta" alumina. In both cases, the exchange data was used to construct a profile of ion concentration as a function of time, thus permitting a diffusion coefficient to be calculated. The diffusion coefficients were inserted into the Nernst-Einstein equation to produce calculated values for the ionic conductivity at the ion exchange temperature. The agreement between these calculated values and the conductivity values extrapolated from a.c. impedance measurements is quite good and serves to demonstrate that divalent cation motion in beta" aluminas is sufficiently rapid to account for the observed conductivities.

Another interesting set of measurements has been performed on mixed monovalent-divalent beta and beta" alumina compositions. Ni et al. (9) investigated the effect of various amounts of Ca^{2+} on the conductivity of mixed $\text{Na}^+ - \text{Ca}^{2+}$ beta" aluminas. They found that even small concentrations of Ca^{2+} dominated the conduction process. Single crystals with as little as 10% Ca^{2+} replacement suffered a loss in conductivity of over 10^2 . It is interesting to note that these slightly exchanged compositions exhibited conductivities comparable to fully exchanged Ca^{2+} beta" alumina. The mixed monovalent-divalent beta aluminas show distinctly different behavior. Studies of $\text{Na}^+ - \text{Cd}^{2+}$ beta alumina indicate that the conductivity actually increases as Cd^{2+} replaces Na^+ . However, in the range 36 to 39% Na^+ replacement, a large and sudden decrease in conductivity occurs with a corresponding increase in the activation energy for conduction. These effects are associated with a change in the Na^+ migration process, from an interstitialcy to a vacancy mechanism (10,11).

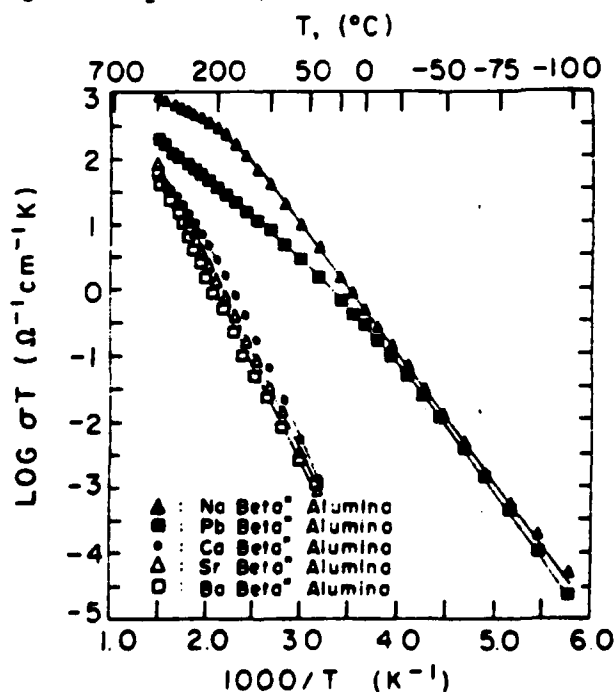
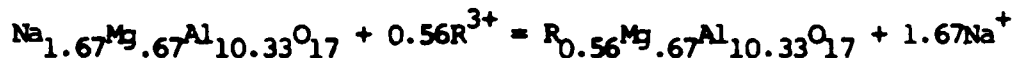


Fig. 2 Conductivity of divalent beta" aluminas compared to Na^+ beta" alumina

III. TRIVALENT BETA" ALUMINAS

We have recently found that trivalent cations can also be exchanged for the Na⁺ ions in sodium beta" alumina. (12) In this case the exchange reaction involves the replacement of 3 sodium ions by one trivalent cation:



Typical conditions for exchange are listed in Table 3. All of the trivalent ions undergo substantial exchange and complete replacement (or within 5%) has been achieved for Gd³⁺, Ni³⁺ and Eu³⁺. These results clearly demonstrate that the beta" alumina structure is capable of supporting trivalent cation motion. X-ray diffraction analysis indicates that the beta" alumina structure is retained after exchange. Detailed results from single crystal X-ray diffraction of Gd³⁺ beta" alumina shows that the Gd³⁺ ions essentially occupy only the mid-oxygen sites. (13) The Gd³⁺ ion is strongly bound to its oxygen neighbors, and the O(5) column oxygens are displaced towards the Gd³⁺ ions by ~ 0.5Å. The bound nature of Gd³⁺ is consistent with our preliminary conductivity values for this composition, i.e., a rather low conductivity at room temperature (less than 10⁻¹¹ ohm⁻¹ cm⁻¹). At higher temperatures, however, the trivalent ions are quite mobile (Fig. 3). Although the conductivity of the trivalent species is less than that of divalent or monovalent ions, its conductivity is still comparable to that of stabilized zirconia. The higher activation energy for Gd³⁺ motion is expected because of the increased difficulty of transporting an ion of greater valence. Nonetheless, we know of no other compounds which permit trivalent cation motion at these temperatures and, at this time, the trivalent beta" aluminas appear to be the first crystalline solids to possess high conductivity for trivalent cations.

IV. CONCLUSIONS AND PROSPECTS

The ion exchange studies clearly establish that the phenomenon of fast ion transport in solids is not limited to monovalent cations but can be demonstrated by multivalent ions as well. It is not known if beta" alumina is unique in this regard or whether other compounds can also support rapid transport of multivalent cations. What is significant technologically is that the multivalent beta" aluminas greatly extend the possibilities for ion sensors based on solid electrolytes to a range of ions which were previously unavailable. It should also be appreciated that the host structure, beta" alumina, is very well suited for sensor applications. The material possesses excellent thermal and chemical stability, and maintains its performance in corrosive environments. High quality beta" alumina ceramics are fabricated routinely and initial efforts to prepare polycrystalline divalent beta" aluminas have been successful (14). The unusual combination of properties offered by the multivalent beta" aluminas including thermal stability, chemical durability and fast ion transport, strongly suggests that novel sensors based on the multivalent beta" aluminas should be actively explored.

Table 3

Trivalent Ion Exchange Conditions

Ion	Melt Composition	Temp(°C)	Time(h)	% Exchange
Gd ³⁺	GdCl ₃	614	5	100
Nd ³⁺	NdBr ₃	720	0.5	95
Eu ³⁺	EuCl ₃	870	20	95
Sm ³⁺	SmCl ₃	700	20	90
Bi ³⁺	BiCl ₃	270	12	70

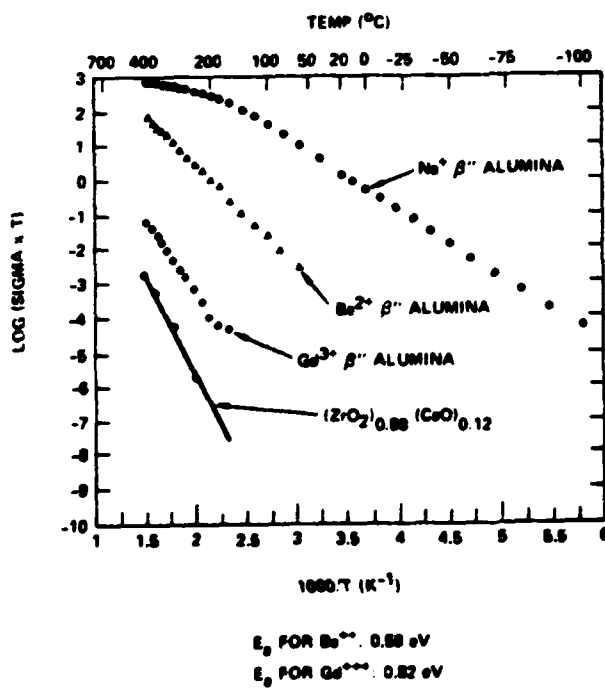


Fig. 3 Conductivity of monovalent, divalent and trivalent beta'' aluminas compared to stabilized zirconia

Acknowledgement

The authors are grateful for the support of this work by the Office of Naval Research (Contract Nos. N00014-81-K-0526 and N00014-83-K-0498) and, at the University of Pennsylvania, by the National Science Foundation (MRL Program No. DMR-7923647).

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